

## POLYURETHANES WITH A DIAMINE-DIAMIDE CHAIN EXTENDER

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### Introduction:

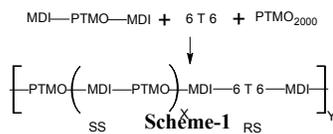
Thermoplastic polyurethanes are interesting materials that combine a good elastic behavior while being melt processable [1]. The thermoplastic polyurethanes are often made from poly(tetramethylene oxide) (PTMO) soft segments (SS) and MDI-butenediol rigid segments (RS). The urethane rigid segments have a random length distribution and with that a broad melting transition and a modulus that is strongly temperature dependant. If the RS is mono-disperse in length the melting transition is sharper and the modulus less temperature dependant [2]. Unfortunately mono-disperse polyurethane segments undergo in the melt transurethane reactions and by that loses its mono-disperse character [2]. Polyurethanes that do not change its polydispersity on transurethane reactions are isocyanate end-capped SS reacted with diamine extenders. These RS are short in length and the content in the polymer low. Due to this they have a very low modulus. Polyurethanes that are also mono-disperse in RS length and resistant to transurethane reactions are isocyanate end capped SS in combination with diamine-diamide extenders [3,4]. The diamine-diamide extenders studied are 6T6 based on hexamethylene diamine (HMDA) [3] and terephthalic acid and 6A6 based on HMDA and adipic acid [4]. These polyurethanes have a high crystallinity of the RS and have a higher RS content than that using a diamine and with that higher moduli of the copolymers. The properties are typical for RS with a mono-disperse segment length like good low temperature flexibility, a modulus that is little temperature dependant, a narrow melting transition and good elastic behavior.

Studied now is MDI end-capped PTMO that is extended with the diamine-diamide 6T6. In this study the concentration of the RS is changed by exchanging 6T6 units for PTMO units. In this way the SS composition is changed from PTMO to PTMO extended with isolated MDI units (-PTMO-(MDI-PTMO)<sub>n</sub>-). What effect this has on the (low temperature) properties is studied.

### Experimental

**Materials.** Dimethyl terephthalate (DMT), hexamethylene diamine (HMDA), anhydrous N,N-dimethyl acetamide, Diethylether, 1,1,1,3,3,3-hexafluoro-isopropanol (HFIP) were purchased from Aldrich and used as received. 4, 4'-methylenebis (phenyl isocyanate) end capped PTMO, M<sub>n</sub>= 2847 g/mol including the MDI groups, was a gift from Crompton. PTMO<sub>2000</sub> was a gift from Dupont. 6T6 was synthesized from DMT and HMDA [5].

**Synthesis of polyurethane with diamine-diamide chain extender.** MDI end capped poly(tetramethylene oxide) (20g, 7.02 x 10<sup>-3</sup> mole) was taken in dry stainless steel reactor which was properly equipped with nitrogen inlet, magnetic coupled mechanical stirrer. First we add 20 ml anhydrous dimethylacetamide (DMAc) in to the reactor and raise the oil bath temperature to 70°C for making a homogeneous transparent mass of prepolymer. After that we add the diamine-diamide chain extender (6T6) which was already dissolved in anhydrous DMAc. Then we increase the temperature to 120°C and reaction was continued for 5hr in inert atmosphere. Solvent stripping was performed initially by applying low vacuum (by using water suction), when most solvent was stripped out then we applied a high vacuum (pressure < 0.3 mbar) for 60 min at 120°C. The reactor was cooled under reduced pressure. The synthesized copolymer was removed from reactor by crushing in liquid nitrogen. Transparent, colorless and tough polyurethane was finally dried for over night in vacuum oven at 50°C. Scheme 1 represents the synthesis of chain extended polyurethanes.



**Compression moulding.** Test samples were prepared by compression molding in a 40 ton Lauffer 40 press. Sample was dried over night in vacuum oven at 50°C. The compression molding temperature was 230°C for 1 min duration at 8.5 MP<sub>a</sub> pressure after four times compressing-decompressing for removing the inside air.

**Viscometry.** The inherent viscosity of segmented polyurethanes were measured in a mixed solvent of phenol and 1,1,2,2-tetrachloroethane (1:1 mol ratio) at 25°C by using a capillary Ubbelohde type 1A. 0.1g/dl concentration solutions were used for viscosity measurement.

**Dynamic mechanical thermal analysis (DMTA).** DMTA spectrums were recorded by a Myrenne ATM3 torsion pendulum at a frequency of 1 Hz and 0.1% strain. Initially the samples were cooled to -100°C and subsequently heated at a rate of 1°C/min. Glass transition of polymer was defined as a temperature at which loss modulus reaches to its maximum value. The flow (T<sub>flow</sub>) temperature is defined as a temperature at which storage modulus reaches to 0.5 MPa. The temperature at which rubbery plateau start is defined as flex temperature (T<sub>flex</sub>) which is generally determined as an intercept of two tangents.

**Tensile.** Stress-strain properties were measured following ISO 37 type 3 on a tensile testing machine (Zwick Z020 universal tensile tester) equipped with a 500N load cell at room temperature with a uniform speed of separation 60mm/min. Extensometers were used for exact strain measurement of polymer samples. Three fold measurements were performed according to the standard at strain rate of 0.4s<sup>-1</sup>.

**Compression set.** The compression set was measured at room temperature and 35°C according to ASTM 395 B standard. Compression was released after 24 h compression at respective measurement temperature. The thickness of the samples was measured after half an hour relaxation. The compression set is defined as

$$\text{Compression set} = \frac{d_0 - d_2}{d_0 - d_1} \times 100 \%$$

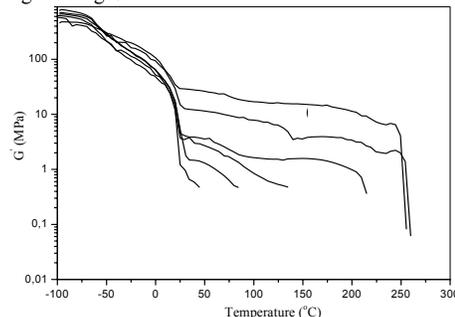
Where  $d_0$  = thickness before compression (mm)  
 $d_1$  = thickness during compression (mm)  
 $d_2$  = thickness after 30min relaxation (mm)

### Result and Discussion

Polyether(bisurethane-bisurea-bisamide) (PUUA) were synthesized from poly(tetramethylene oxide) (PTMO<sub>2000</sub>) end capped with MDI (M<sub>n</sub>= 2847 g/mol including MDI groups) a uniform diamine-diamide chain extender 6T6 and PTMO<sub>2000</sub> segments with a molecular weight of 2000 g/mol. In order to vary the RS concentration some of the 6T6 was exchanged for PTMO<sub>2000</sub>. For percentage of RS concentration we considered those MDI groups which were connected with diamine-diamide extender only. The MDI groups that were reacted with PTMO<sub>2000</sub> formed (-PTMO-(MDI-PTMO)<sub>n</sub>-) SS. The polymerizations were carried out at 120°C to minimize the side reactions. The copolymers had all a moderately high inherent viscosities.

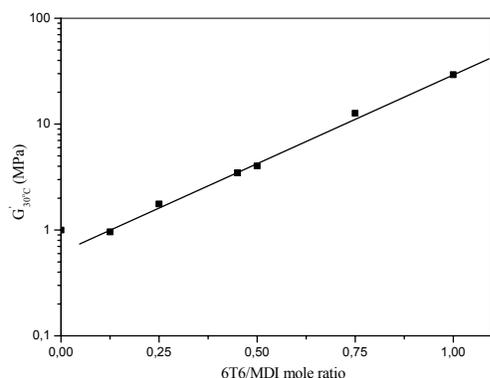
**Morphology Study by AFM.** The (surface) morphology of these segmented polyurethanes was analyzed by tapping mode, measuring the phase angle. The hard phase appears as light regions in these phase images. At the 10 wt % RS content sample fine ribbon like structure was observe. The RS have thus crystallized out in ribbons with a high aspect ratio.

**DMTA results.** Thermo-mechanical properties of the polymers were measured by DMTA. Although the segmented polyurethanes are at high temperatures thermally unstable the DMTA spectrum could well be recorded as in this test the strain was very low (0.1 %) and thus not sensitive to molecular weight changes.



**Figure 1.** Change in storage modulus with temperature at different 6T6/MDI ratios: O (1); □ (0.75); Δ (0.50); ◇ (0.45); + (0.25); \* (0.125).

The storage modulus ( $G'$ ) was determined as function of RS content (Fig. 1). Three transitions are observed a  $T_g$  of the SS, a  $T_m$  of the PTMO and a  $T_m$  ( $T_{flow}$ ) of the RS. The  $T_g$  of all the copolymers was low and did not change with composition. The  $T_m$  of the PTMO as judged by the  $T_{flex}$  temperature hardly changed with SS composition. The modulus of the rubber plateau was little temperature dependent, however as the  $T_{flex}$ - $T_{flow}$  window decreased the slope increased. The melting transition of the RS is very sharp. The low  $T_g$ , the little temperature dependant rubber modulus and the sharp RS melting transition are typical for systems with mono-disperse RS. Thus even after melt pressing the RS in the copolymers seem to have mono-disperse segment length. With increasing RS content the storage modulus at room temperature increases strongly and the  $T_{flow}$  is shifted to higher temperatures. The storage modulus increased linearly with the log of the modulus (Fig. 2).



**Figure 2.** Effect of RS concentration on room temperature storage modulus.

Such a strong increase cannot be explained by a changing cross link density and must be due to the reinforcing effects of the phase separated RS. The RS have crystallized in nano-ribbons with a high aspect ratio (Fig. 1) and these nano-ribbons are expected to be the main reason for the strong increase in modulus. The fact that the (log) modulus increases linearly with the RS concentration also suggest that the crystallinity of the RS is not lowered by having urethane groups in the SS.

The  $T_{flow}$  decreases strongly with decreasing RS content. Such a decrease is often observed for segmented block copolymers with mono-disperse segment length. This decrease has been explained as being due to the solvent effect of the SS and depends on the SS content and the SS interaction [6]. In the studied system the decrease in  $T_{flow}$  is strong and this suggest that there is a strong interaction between the urethane-urea-amide RS and the PTMO-MDI-PTMO SS.

**Tensile properties.** The tensile measurements were on molded bars cut into a dumbbell shape samples according to ISO 37 type 2 specification. Measured were the Young's modulus, the yield stress and yield strain. As the samples were far from optimal the fracture properties are not given. The results are summarized in Table 1.

**Table 1** Tensile properties of PUUA as function of 6T6/MDI ratio

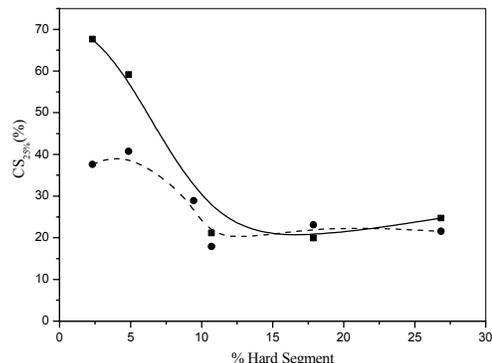
Ratio <sup>1</sup>	RS (wt %)	Length SS	G-Modulus	E-Modulus	$\sigma_{yield}$ (MPa)	$\epsilon_{yield}$ (%)	CS (%) 20°C	CS (%) 35°C
1	26.9	2350	29	81	4.8	35	25	22
0.75	17.9	4000	13	27	3.2	37	20	23
0.50	10.7	7200	4	14	2.2	53	21	18
0.45	9.4	9800	3.4	6.2	2.1	76	36	29
0.25	4.9	16900	1.8	4.2	1.5	110	59	41
0.125	2.3	36300	1.0	3.0	0.6	117	68	38

<sup>1</sup> mol ratio 6T6/MDI

The Young's modulus increased with the RS content and was 81 MPa for 26.9 wt % RS.

The Young's modulus increase had the same trend as the storage modulus increase but at a higher level. The yield point was determined by the Considere construction. The yield stress increases (linearly) with the RS content. The yield strain is high for low RS contents and decreases with contents.

**Compression Set.** From compression set measurement we can get an idea about the elastic behavior of the segmented block copolymer. Lower compression set value indicates the more elastic behavior. The elastic properties are reduced if the PTMO has at the measuring temperature a crystalline phase and if the melting temperature of the RS is nearing the measuring temperature. At the higher RS contents the CS at 20 °C is about 20%, however at the very low contents the CS values are much higher (Fig. 3).



**Figure 3.** Compression set values as function of RS content: ■ 20 °C; ● 35°C.

If the CS was measured at 35°C the high RS content copolymers still had low CS values and the values for the very low RS content were now lower. It thus seems that the CS at the very low RS is at 20°C limited by a crystalline PTMO phase. The fact that the CS values at 35 °C for the very low RS contents are not very low suggest that possibly the melting temperature of the RS is now interfering or that to less than two RS are in the polymer chains.

## Conclusions

A series of polyurethanes were prepared with mono disperse RS from isocyanate (MDI) end capped poly(tetramethylene oxide) and a diamine-diamide extender. The RS have crystallized out in nano-ribbons with a high aspect ratio. These copolymers have even after melt processing a mono-disperse character. The  $T_g$  of the SS is low, the modulus is little temperature dependant, the RS melting transition is sharp and the CS values are low. With increasing RS concentration the modulus increases strongly and so also the melting temperature. Remarkable is that MDI units that extend the PTMO segments hardly influence the  $T_g$  of the polyether phase, the  $T_{flex}$  and the modulus of the copolymers.

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## References

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